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Seasonal variability of monoterpene emission factors for a ponderosa pine plantation in California

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Abstract

Monoterpene fluxes have been measured over an 11-month period from June 2003 to April 2004. During all seasons ambient air temperature was the environmental factor most closely related to the measured emission rates. The monoterpene flux was modeled with the exponential relation suggested by Tingey et al. (1980) and Guenther et al. (1993); a basal emission of 1.0 μmol h^{-1} m^{-2} (at 30°C, based on leaf area) and a temperature dependence (β) of 0.12°C^{-1} reproduced measured summer emissions well but underestimated spring and winter measured emissions by 60–130%. The total annual monoterpene emission may be underestimated by ~50% when using a model optimized to reproduce monoterpene emissions in summer. The long term dataset also reveals an indirect connection between non-stomatal ozone and monoterpene flux beyond the dependence on temperature that has been shown for both fluxes.

1. Introduction

Biogenic terpene emissions are very reactive and thus alter the atmosphere's oxidation capacity on local scales. In addition, terpene oxidation products like acetone and formaldehyde (Wisthaler et al., 2001; Lee et al., 2005a) are potent sources of HO_x radicals, and the long lifetime of acetone makes it an important HO_x source in the upper troposphere. Besides the important role biogenic terpenes play in gas phase chemistry, their impact also extends to heterogeneous air chemistry. Although Went (1960) linked the formation of "blue haze" over coniferous forests to the biogenic emission of monoterpenes over 40 years ago, it wasn't until recently that terpenes received their due attention with respect to their role in secondary organic aerosol formation (SOA). O'Dowd et al. (2002) reported that nucleation events over a boreal forest were driven by condensation of terpene oxidation products. For the past few years we found increasing evidence that the total terpene emission at our Blodgett forest site is larger than typically measured over the forest canopy (Kurpius and Goldstein, 2003; Goldstein et

ACPD

5, 8791–8810, 2005

al., 2004); other groups reported similar inferences from observations in other ecosystems (Ciccioli et al., 1999; Di Carlo et al., 2004). Recently, we observed unidentified chemical species with highest concentrations just above the canopy; these compounds are likely oxidation products of very reactive terpenoid compounds suggesting that the unaccounted terpene emissions may be 6–30 times the monoterpene emission measured at the top of the forest canopy (Holzinger et al., 2005).

Plant species that store terpenoid compounds in resin or other pools emit these compounds mainly as a function of temperature. Regional and global emission models for terpenoid compounds are typically based on this relationship and are parameterized with basal emission rates and temperature response factors obtained from field measurement campaigns in the respective ecosystems which rarely last more than a month. While other parameters like mechanical disturbance (Yatagai et al., 1995), humidity (Schade et al., 1999), and leaf expansion (Kuhn et al., 2004) are known to influence terpene emission it is not known what fraction of the total terpene emission can be attributed to additional parameters. We measured monoterpene fluxes above the forest canopy for almost 11 months. Our results indicate enhanced monoterpene emissions in spring and winter compared to summer. A model parameterized to fit summer observations would underestimate the measured monoterpene emission by roughly 50% over the course of the study.

2. Experimental

The study was performed at the Blodgett forest site on the western slope of the Sierra Nevada, California (38.90° N, 120.63° W, and 1315 m elevation). The plantation is located 75 km down-wind (northeast) of Sacramento and receives anthropogenically impacted air masses rising from the valley below during the day. The site was planted with Pinus ponderosa L. in 1990, interspersed with a few individuals of Douglas fir, white fir, California black oak, and incense cedar. Average tree height was 4.8 (median) in 2003; the canopy height was 6.4 m, a height exceeded by 20% of the trees. The un-

derstory was composed primarily of manzanita (Arctostaphylos spp.) and whitethorn (Ceonothus cordulatus) shrubs. Local biogenic VOC emissions and the effect of transported air pollution are discussed in detail in some of our earlier work (Lamanna and Goldstein, 1999; Schade and Goldstein, 2001; Dillon et al., 2002).

The experimental setup was identical to the one which was described by Lee et al. (2005b), and for detailed information on the setup and a discussion of uncertainties and errors we refer to this paper. Total monoterpenes have been measured with proton-transfer-reaction mass-spectrometry (PTR-MS) which was described by Hansel et al. (1995), a detailed review of this technique is given by Lindinger et al. (1998). The gas inlet was located next to a sonic anemometer at a height of 12.5 m above the ground (~4–7 m above the top of the trees). Through 1/4″ ID Teflon PFA tubing we pulled sample air to the PTR-MS instrument which was located in an air-conditioned container next to the tower. The flow through the sample line was stabilized at a rate of 10 standard liters per minute by a flow controller (MKS instruments). One measurement cycle was completed in 0.5 s which included 0.2 s integration time on both mass 137 (protonated monoterpenes), and mass 81 (monoterpene fragment ion); the remaining 0.1 s were needed for acquisition of the primary ion signal and the 3-dimensional wind field. Monoterpene mixing ratios were calculated from the ion signals at mass 137 and mass 81, the monoterpene fluxes were calculated according to the eddy covariance (EC) method. During the whole period gas standards were measured every 10 h to correct for any kind of drift and uncertainties in the reaction rate constants. We sequentially switched between 3 gas standard cylinders (Scott Marrin Inc, and Apel & Riemer) containing pure nitrogen with low mixing ratios (a few parts per million) of α-pinene, β-pinene, and a mix of α-pinene, Δ-3-carene, and d-limonene (5:5:2), respectively. The standard and sample gas streams were mixed under turbulent conditions, so that the PTR-MS was calibrated against standard concentrations in the range of 1–20 nmol/mol. The overall error for monoterpene concentrations and fluxes should be less than ±20%, and ±30%, respectively.

Most of the analysis presented in this paper was done with emission rates that were

normalized to leaf area rather than soil surface. These were simply calculated by dividing the measured flux (based on soil surface) by the leaf area index (LAI), the evolution of which is presented in Fig. 1. LAI is calculated using data from an inventory which is taken every year in early spring (before the growing season starts) along the footprint area. Based on these inventories the LAI for the different needle age classes is calculated from allometric equations presented in Xu et al. (2001). The evolution of LAI during the growing season is reconstructed by assuming that the dynamics of leaf area followed needle elongation, similar to Misson et al. (2005).

3. Results

3.1. Seasonality of monoterpene emissions

Figure 2a shows 30-min average values of the physical parameters photosynthetic active radiation (PAR), air temperature, and precipitation for the 11-month (8 June 2003 to 14 April 2004) measurement period. The radiation and temperature timelines include only data taken between 10:00–16:00 PST (Pacific Standard Time; equals coordinated universal time, UTC, minus 8 h); thus day to night variations are not represented in the graph. In accordance with regional climatology most precipitation occurred during the winter months; however, in summer 2003 there were some rain events in July and August. The end of the summer season is marked by a sharp drop in day-time air temperatures from 26°C on 28 October to 0°C on 30 October coinciding with the first snowfall of the season.

Half-hour day-time (PAR>200 μmol m^{-2} s^{-1}) monoterpene flux (MT_{flux}) data are shown in Fig. 2b (n=1390). We consider the colored data-points (n=710) in Fig. 2b to be the most representative and reliable; they passed two general filters: (i) the wind direction came from the main footprint area of the tower (130°–290°), and (ii) the turbulence parameter, u*, was above a conservative threshold value of 0.3 m s^{-1}, as the eddy-covariance method becomes less reliable when turbulence is low (Goulden et al.,

ACPD
5, 8791–8810, 2005

1996).

A scatter plot of the representative subset of data and air temperature (Fig. 3) shows that monoterpene flux exponentially increased with ambient air temperature, thus Fig. 3 suggests that even over the course of a year temperature is the main environmental parameter controlling the emission rate. However, Fig. 3 also suggests that other parameters must impact emissions since the variability of measured monoterpene fluxes at any given temperature exceeds the experimental uncertainty. The monoterpene flux was modeled (black line in Fig. 3) using the exponential relationship $MT_{flux}=F30\ e^{(\beta(T-30))}$, were F30 is the basal emission rate at 30°C, T the temperature, and β the temperature response factor. The optimized values, obtained by non-linear least square fitting, were $1\,\mu mol\,m_{leaf}^{-2}\,h^{-1}$ and $0.08°C^{-1}$ for F30 and β, respectively. Modeled and measured monoterpene fluxes are correlated but the relatively poor correlation coefficient ($r^2=0.46$) is another indicator of additional parameters influencing monoterpene emissions.

We were not able to improve the correlation significantly with more advanced models that, in addition to temperature, included parameters like solar radiation, humidity, leaf wetness and others; apparently monoterpene emissions are not generally triggered by any of the many other parameters that we routinely monitor at our site. To further investigate the seasonality of monoterpene emissions we analyzed the temperature dependence by looping through the data in one-day steps and forming subsets including the data of that particular day, the previous and the following days. If the subset contained at least 6 data points, the corresponding times comprised a period of 24 h or more, and the corresponding temperatures comprised a range of 2.5°C or more, we modeled the subset by means of non linear fitting. Data points that could be modeled and were reasonably correlated with observations ($r^2<0.25$) were separated and the $F30_i$ and β_i parameters were compiled. In Fig. 2b these 440 data points are plotted in purple, whereas the 270 data points plotted in blue squares could not be reasonably modeled.

Example scatter plots of modeled and measured MT_{flux} over short time periods are

ACPD
5, 8791–8810, 2005

shown in Figs. 4a–f; data points included in Fig. 4 are plotted in light purple squares in Fig. 2b. Subsets c and d represent typical summer and subset f represents typical winter conditions. Non linear fitting of these subsets yielded basal emission rates (F30) and temperature response factors (β) similar to those obtained from fitting the entire dataset. Both the F30 and the β parameter were significantly higher in models for subsets a, b, and e. Measurements from Subset a date from 8–10 June and represent typical springtime measurements; high monoterpene emission was observed on days following rain events late in July and early August (subset b) and after the first snowfall on 31 October (subset e).

A more general picture is obtained from Fig. 5 which is a scatter plot of measured and modeled MT_{flux} of all subsets versus ambient air temperature. Measurements that could be modeled according to the procedure described above are printed as grey solid squares; those that could not be modeled are displayed as grey open circles. All model results representing typical summer or winter conditions are positioned along an "exponential band" and are displayed as black solid circles in Fig. 5. Model results outside the "band of normal" could either be attributed to precipitation events or they represent times early in the growing season. Precipitation events that marked the end of a longer period without rain or snowfall were followed by bursts of monoterpene emissions, but the emission capacity of the ecosystem was not permanently enhanced when rain or snowfall occurred: no significant emission burst followed the rain event of 31 August which was preceded by several other rain events (see Fig. 2); similarly, no significant bursts followed the many snow or rainfalls in November after the first one on 31 October. In addition to the enhanced emission following precipitation events a seasonal cycle is apparent in Fig. 5: monoterpene fluxes in spring 2003 were much larger than in any other season, and in early spring 2004 this cycle began to start over again.

The insights gained from fitting short time periods allow to improve the model performance over longer periods: we formed another subset of data including all typical summer and winter data, and excluding precipitation events and spring data. Values

ACPD
5, 8791–8810, 2005

of 1 μmol m_{leaf}^{-2} h^{-1} and 0.12°C^{-1} for model parameters F30 and β, respectively, were obtained from fitting this subset. Since we excluded all non-typical and unreliable data points we consider these values to be the most accurate and representative overall model parameter for our site, which is also expressed by the high correlation (r^2=0.74) between measured and modeled MT_{flux}. The modeled MT_{flux} is represented by the solid green line in Fig. 5. Comparing the overall model with the results from the short time period modeling (Fig. 5) reveals an additional seasonality – more subtle than the enhanced emission during spring: in accordance with measurements, most model results adapted to short time periods in winter predict about 50–100% larger monoterpene emissions than the overall model at the given temperature range. In contrast, during summer the short time period modeling results appear symmetrically scattered around the results of the overall model (green line in Fig. 5).

In the following we will evaluate the overall model with respect to the actual measurements over the course of the year in order to quantitatively assess the seasonality. It is useful to define following time periods: "all": 8 June 2003 to 14 April 2004, "spring 2003": before 28 June 2003, "summer": 28 June to 29 October 2003, "winter": 30 October 2003 to 28 February 2004, "spring 2004": after 28 February 2004, "rain event", 2–6 August 2003, and "first snow event": 30 October to 7 November 2003. The mean modeled and measured monoterpene flux for these periods is presented in Table 1. The measured exceeded the modeled MT_{flux} in each of the defined periods. The best agreement was obtained for the summer data. On average measured values were 9% above the modeled ones; the disagreement decreased to 5% when data during the rain event were excluded. Modeled and measured summer-means are in excellent agreement (better than ±0.5%) when data not reasonably correlated with temperature were excluded (not shown). During winter and spring the actual monoterpene emissions were 60–130% higher than the model had predicted; the enhancement due to the rain events are also encompassed by this range, and the ∼300% enhancement following the first snow fall is striking but has to be interpreted in the context of very low modeled emissions. With all data put together, the mean-measured flux was 30% higher than

ACPD
5, 8791–8810, 2005

the mean-modeled flux. Considering that spring and winter data are underrepresented in our dataset (see Table 1), the difference between modeled and real mean-annual monoterpene emission likely is larger than this number. The annual mean MT_{flux} can be calculated according to

$$F_{annual} = (0.5 \times F_{spring2003} + 0.5 \times F_{spring2004} + F_{summer} + F_{winter})/3 \quad (1)$$

when the year is equally divided into spring, summer and winter season. Equation (1) yields values of 0.43 and 0.29 μmol m_{leaf}^{-2} h^{-1} for real and modeled mean-annual monoterpene emissions, respectively, so our data suggest that the best model for the Blodgett site underestimates the real emissions by ~50% over the course of a year.

3.2. Monoterpene and non-stomatal ozone flux

We also used the long term dataset to test if there was a correlation between monoterpene emission and non-stomatal ozone flux into the canopy. In earlier work we hypothesized that during summer a large fraction of the ozone flux into the canopy was due to chemical reaction of ozone with very reactive terpenoid compounds that were emitted through similar mechanisms as the monoterpenes but at larger quantities (Kurpius and Goldstein, 2003; Holzinger et al., 2005). Figure 6 depicts canopy scale MT_{flux} based on ground area (as opposed to leaf surface area in previous figures) versus ambient air temperature in solid grey squares. The color code indicates the non-stomatal ozone flux ($O_{3,flux-ns}$, calculated according to Kurpius and Goldstein, 2003) and was derived as follows: we extracted times of MT_{flux} measurements within individual temperature-flux bins; whenever 4 or more $O_{3,flux-ns}$ data points existed, that grid square was colored according to the mean of the 4 or more $O_{3,flux-ns}$ values. Figure 6 clearly confirms the discovery of Kurpius and Goldstein (2003), which was that the $O_{3,flux-ns}$ scales with temperature. In addition to the correlation with temperature, Fig. 6 reveals that at a given temperature $O_{3,flux-ns}$ into the canopy was larger when monoterpene emissions were higher. This is easily illustrated with round figures obtained from Fig. 6: at times with a temperature 27°C and a MT_{flux} of either ~3 or ~7 μmol $m^{-2}h^{-1}$ the corre-

sponding mean $O_{3,flux-ns}$ was ~25 and ~40 μmol $m^{-2}h^{-1}$, respectively. The qualitative connection between $O_{3,flux-ns}$ and MT_{flux} strongly suggests that along with the emission of monoterpenes large amounts of other substances are released that react with ozone and cause the observed chemical $O_{3,flux-ns}$. Thus Fig. 6 supports the hypothesis that the oxidation products reported by Holzinger et al. (2005) are products from such ozone-terpenoid reactions.

4. Conclusions and implications

Most regional and global air chemistry models calculate monoterpene emission using the same relation we used for our analysis (MT_{flux}=F30 $e^{(\beta(T-30))}$); parameters F30 and β are defined for different ecosystems and usually no additional seasonality is taken into account. The parameterization of the models is based on availability of experimental data; as for monoterpene emission the F30 and β values for many ecosystems come from field experiments that were performed during summer. Our 11-month field study shows, however, that the actual emissions in spring and winter are 60–130% higher than this approach would yield. Over the course of a year, the total monoterpene emission could be underestimated by 50%. Besides ambient air temperature actual monoterpene emissions are influenced by additional parameters that play important roles and should be accounted for in models, particularly when modeling winter and spring emissions. Our results suggest that short term flux measurements are not sufficient to characterize an ecosystem's monoterpene emission. More data covering different seasons and environments would help to improve the parameterization of chemistry models.

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ational support, and Sierra Pacific Industries for use of their land and assistance in field site operations.

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Table 1. Mean monoterpene flux (modeled and measured) in μmol m_{leaf}^{-2} h^{-1}.

All data (blue & purple in Fig. 2b)									
	all	spring 2003	spring 2004	summer	Summer excluding rain event	rain event	winter	winter excluding first snow event	first snow event
Modeled	0.37	0.36	0.21	0.51	0.53	0.29	0.06	0.06	0.05
measured	0.48	0.83	0.39	0.56	0.55	0.64	0.11	0.10	0.21
# number of data	710	97	44	403	375	28	166	144	16
%-difference	31	134	89	9	5	121	87	61	333

ACPD
5, 8791–8810, 2005

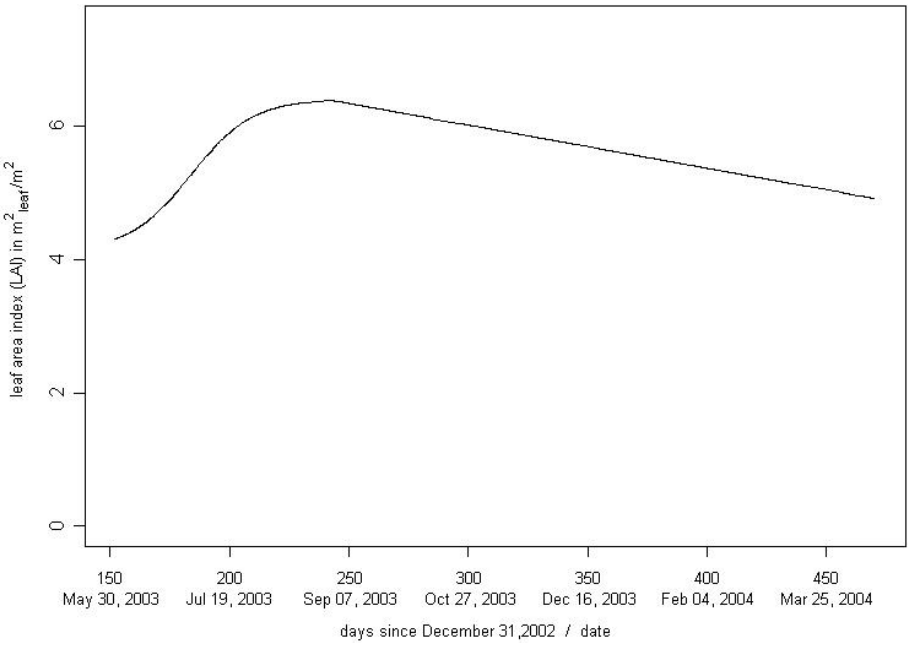

Fig. 1. Leaf area index (LAI) over the course of the study.

ACPD
5, 8791–8810, 2005

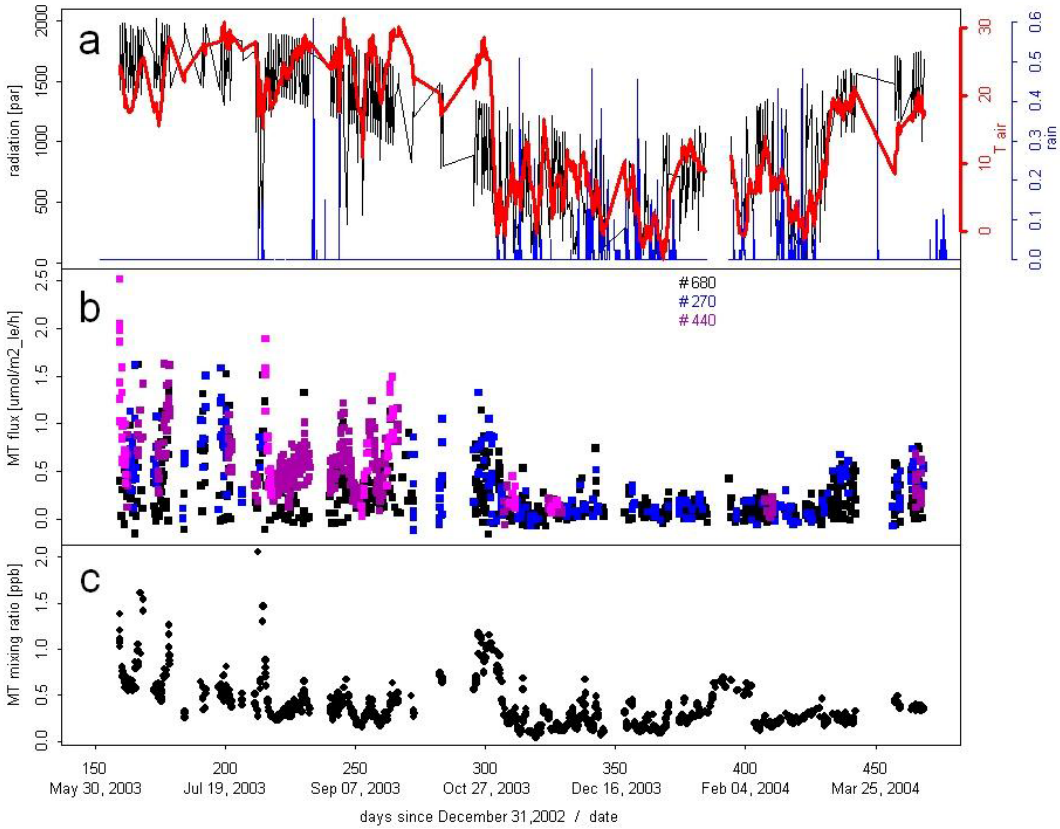

Fig. 2. 30-min average values of **(a)** photosynthetic active radiation (PAR), air temperature, precipitation, **(b)** day-time monoterpene flux, and **(c)** monoterpene mixing ratio in nmol/mol. Panels (a) and (c) include all data from 10:00–16:00 PST. See text for color-code classification of monoterpene flux data.

ACPD
5, 8791–8810, 2005

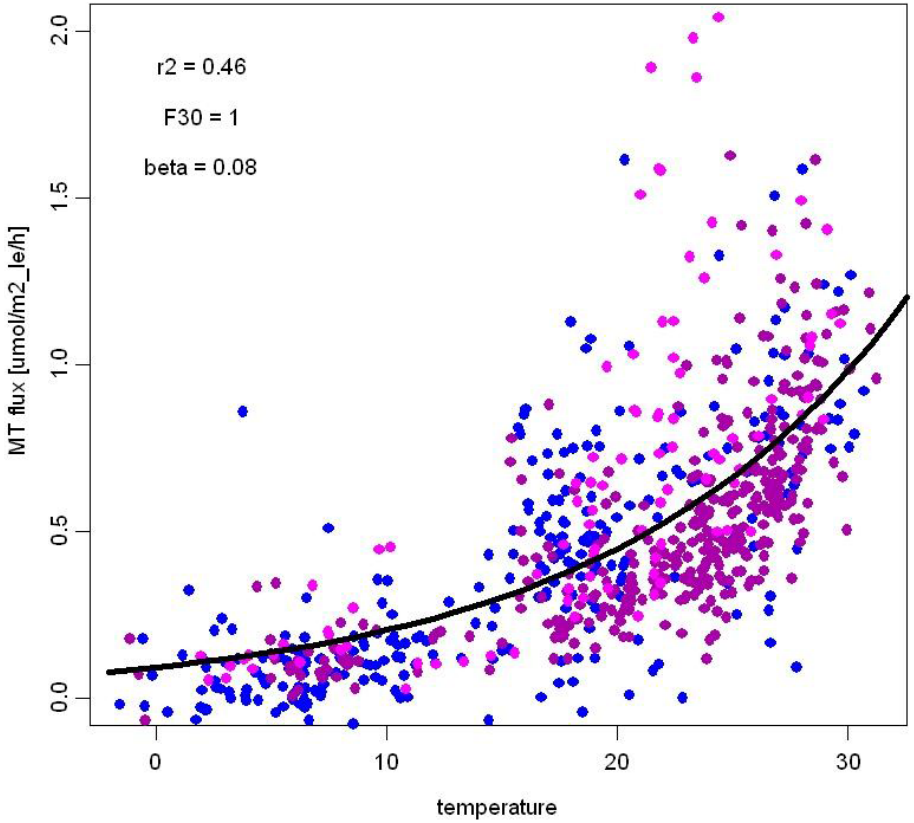

Fig. 3. Scatter plot of ambient air temperature and monoterpene flux including all reliable daytime data under representative wind conditions. The rather poor correlation between modeled and measured monoterpene fluxes (r^2=0.46) indicates other emission controls in addition to temperature.

ACPD
5, 8791–8810, 2005

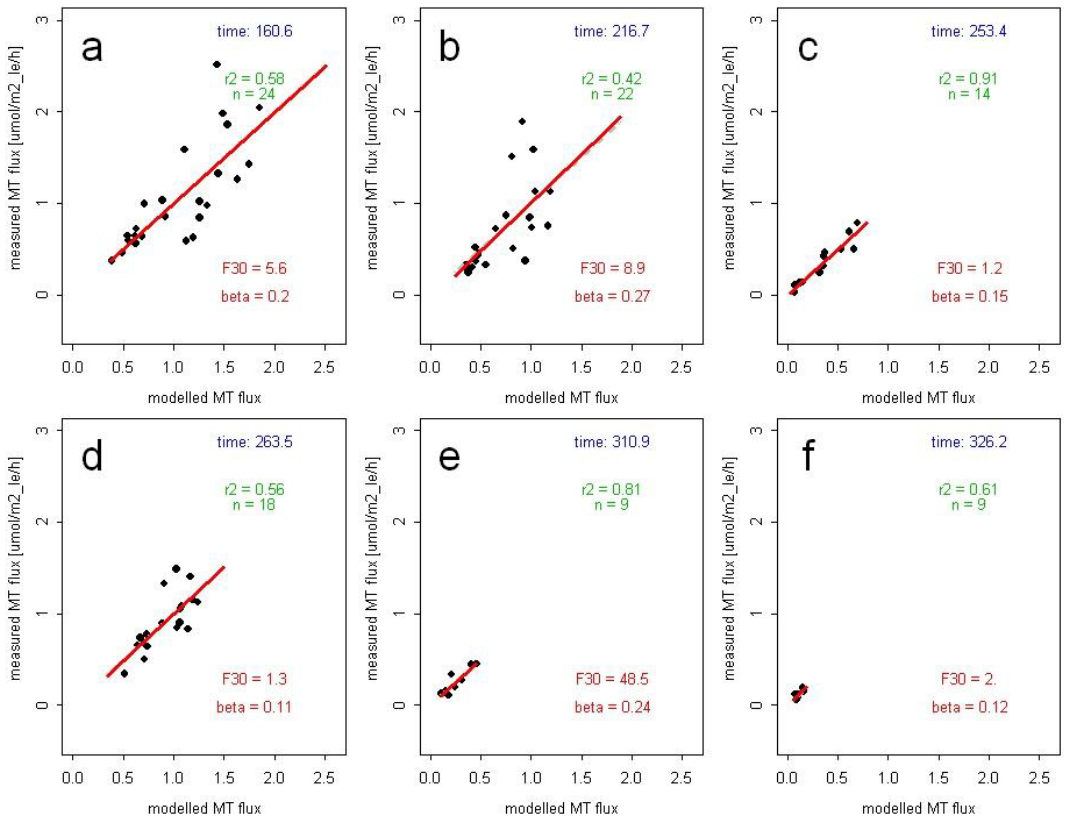

Fig. 4. Example results of models optimized to reproduce measurements of short time periods of 2–3 days. While most model parameters were within the expected range **(c, d, and f)**, others were significantly enhanced **(a, b, and e)**. The higher monoterpene emissions were observed after precipitation events and in spring.

ACPD
5, 8791–8810, 2005

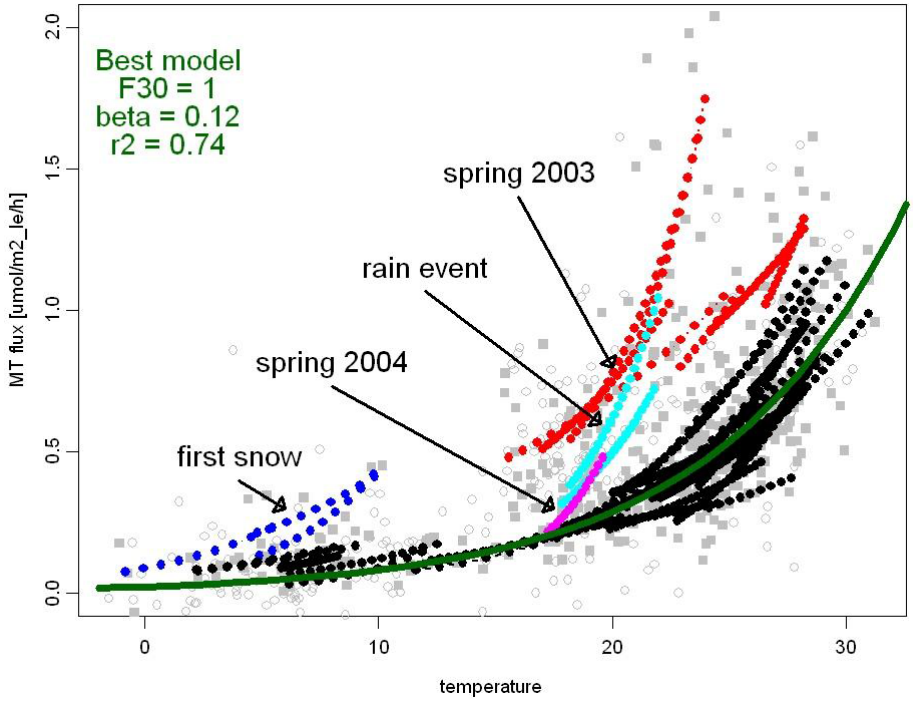

Fig. 5. Measured monoterpene flux (grey symbols) and model results. All results from short time period modeling are included. The best overall model for our site (represented by the green line) is well correlated with measurements (r^2=0.74).

ACPD
5, 8791–8810, 2005

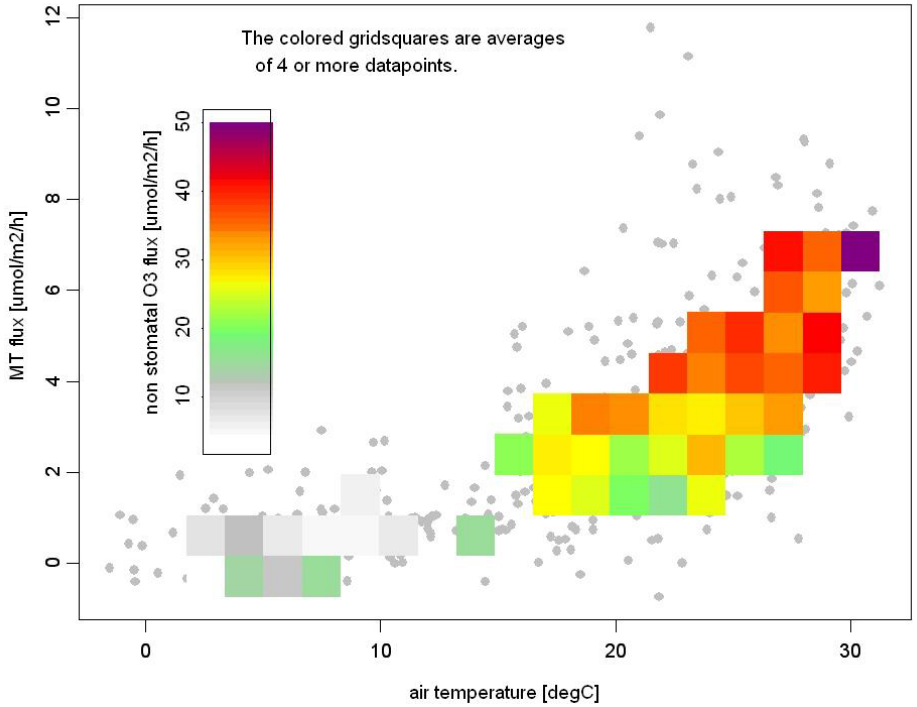

Fig. 6. Scatter plot of ambient air temperature and monoterpene flux superimposed by grid squares color-coded with the corresponding mean non-stomatal ozone flux. At a given temperature the non-stomatal ozone flux into the canopy tends to be higher at times of high monoterpene emissions; thus this plot reveals a connection between those two fluxes that is beyond their mutual dependence on temperature.

ACPD
5, 8791–8810, 2005